Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

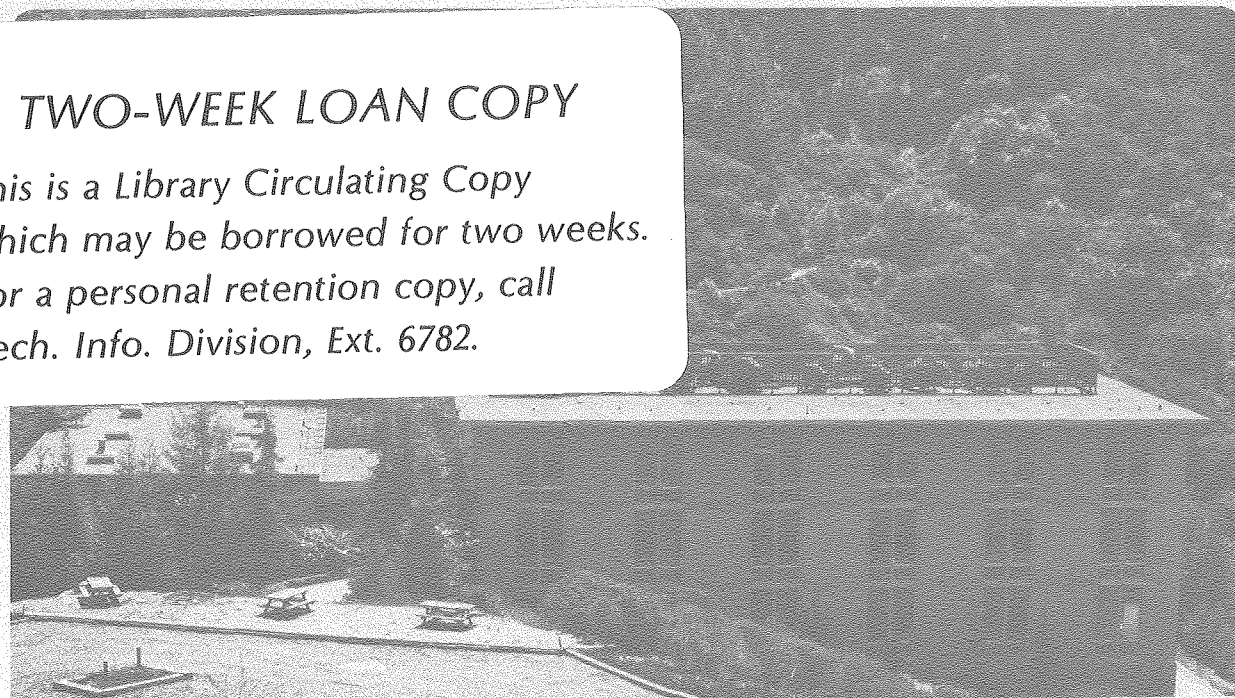## Materials & Molecular Research Division

FOURIER-TRANSFORM ANALYSIS OF NORMAL PHOTOELECTRON
DIFFRACTION DATA FOR SURFACE-STRUCTURE DETERMINATION

Z. Hussain, D.A. Shirley, C.H. Li, and S.Y. Tong

October 1980

DISCLAIMER

FOURIER-TRANSFORM ANALYSIS OF NORMAL PHOTOELECTRON DIFFRACTION DATA FOR SURFACE-STRUCTURE DETERMINATION

Z. Hussain, D.A. Shirley
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, California 94720

C.H. Li,[*] and S.Y. Tong
Surface Studies Laboratory
and
Department of Physics
University of Wisconsin
Milwaukee, Wisconsin 53201

ABSTRACT

A direct method for surface-structure determination from normal emission photoelectron diffraction (NPD) data is presented. Fourier transforms of the calculated NPD intensities yield peaks at adsorbate-substrate normal interlayer distances. Applications are demonstrated using theoretical NPD curves for the Se/Ni system calculated by dynamical theory. These results show that interplanar spacings between the overlayer and as many as four substrate layers could be determined with an accuracy of better than 2%.

[*]Present address: Department of Physics, National Tsing Hua University, Hsinchu, Taiwan, Republic of China.

Following the prediction by Liebsch[1] that diffraction effects are present in photoemission from adsorbate-atom core levels, such effects have been observed in several experimental configurations.[2-4] In each case comparison of experimental results with curves derived from microscopic theory based on certain surface structures[5] showed good agreement, thereby establishing photoelectron diffraction (PD) as a technique for structure determination. Unfortunately, PD data analysis appeared to require a scattering-theory computation of complexity up to the LEED level for each trial structure. In this Letter, however, we propose a direct method for analysis of normal photoelectron diffraction (NPD) data which is independent of model calculations. This method is based on Fourier transformation of NPD intensity curves to yield peaks in the transform at perpendicular distances $d_\perp + nb$, n = 0,1,2,... Here $d_\perp$ is the adsorbate-substrate spacing and b is the substrate interlayer spacing. Fourier-transform NPD (FTNPD) is thus comparable to EXAFS in its simplicity of analysis. The validity of FTNPD is tested by extensive Fourier analysis of theoretical NPD curves. Arguments are presented to show that FTNPD is less dependent on phase shifts than is EXAFS, and the reasons for perpendicular distances dominating the transform are discussed.

First we note some similarities between NPD and EXAFS, in which both differ from LEED. The intensity-versus-energy (I/E) curve in NPD is similar in appearance to either a LEED I/V curve or an EXAFS absorption curve. However, like the latter, NPD is atom-specific. In fact, both the NPD and EXAFS I/E curves result from (photoelectric) excitation of an atomic core level. Most of the diffractive structure in an NPD (EXAFS) curve carries information about the distance from the source atom to other planes (atoms). For both NPD and EXAFS, the diffractive structure

appears as sinusoidal modulation of the photoexcitation curve, and for both cases phase coherence between the scattered wave and the primary unscattered wave is provided by their common origin--the source atom. A different mechanism exists in LEED, which is not atom-specific and for which coherence must be provided by long-range order over 10^2 - 10^3Å in the sample. Just as in EXAFS, where multiple scattering effects are unimportant and/or average out and single-scattering theory prevails,[6] the modulation pattern in NPD at higher kinetic energies depends largely on single back scattering. In fact Li and Tong[7] have shown that only a single backscattering event need be considered to calculate NPD curves for kinetic energies in the 100-400 eV range. Finally, in NPD, as in EXAFS, the periodicity in k space of the sinusoidal modulation increases with decreasing $d_\perp$ where the theoretical curves are calculated over a small range of $d_\perp$. These similarities suggest that Fourier transformation of NPD I/E curve might yield distances directly, as in EXAFS.

To test this hypothesis we have taken the "experimental" approach of computing I/E NPD curves for the Se(3d) orbital in two known structures: $\sqrt{3}$ x $\sqrt{3}$ R30° Se/Ni(111) and p(2x2) Se/Ni(001). These I/E curves were then Fourier transformed to ascertain whether the "input" interplanar spacings would yield features in the transforms. By varying the value of $d_\perp$ for each structure we also tested the first derivative relationship of the input and derived distances. As discussed below, the agreement was very good to excellent in a total of six structures, or 21 interplanar distances, and the first derivatives showed excellent agreement.

Before discussing the detailed results, two aspects of our approach

deserve comment. First, it would be aesthetically more satisfying to derive structural features from a Fourier analysis of the theoretical I/E curves analytically, rather than computationally. Unfortunately an analytical theory has thus far proved to be evasive, although further work on this problem is continuing. Perhaps the results presented below will stimulate additional theoretical activity.

The other aspect is the use of theoretical rather than experimental I/E curves. This choice is supported by two facts. Wherever comparison is available between experiment and theory--about ten cases--the agreement is very good.[8] Also for at least two cases, Fourier transforms of experimental data show peaks at appropriate distances in spite of very limited data ranges,[9] in accord with the conclusions given below. Two factors strongly favored using theoretical, rather than experimental, I/E curves. First, $d_\perp$ could be varied at will, providing a much more sensitive test. Second, the "data" range could be extended in energy at will, again making the test more stringent and meaningful. The results indicate the value of making extra efforts to extend the experimental range of NPD.

Figures 1(a) and 2(a) show the theoretically calculated[7] normalized NPD intensity

$$\chi(k) = (I-I_0)/I_0$$

plotted against k for the two Se/Ni systems. The intensity I_0 is a smooth atomic Se(3d) background, and I is the total intensity expected in an NPD experiment. In deriving $\chi(k)$ from calculated I/E curves (taking E as the electron kinetic energy), the free-electron relation

$$\vec{|k|} = \left[\frac{2m}{\hbar^2} (E+V_0) \right]^{1/2}$$

was assumed. Thus the effective inner potential V_0 sets the zero of

the energy scale. In Fourier transform EXAFS data analysis, V_0 is taken

as an adjustable parameter: we have followed this practice. Lee and

Beni[10] showed for EXAFS data analysis that the imaginary part of the Fourier

transform, $ImF(r)$, is a symmetric function peaked at the neighbor distance,

which should coincide with the peak of the absolute value, $F(r)$, of the

transform. The condition that $ImF(k)$ and $F(r)$ should peak at the same

distance is commonly used to choose the "zero" of the energy scale in

EXAFS. An alternate method for determining the bond distances reliably

in EXAFS by Fourier analysis has been discussed by Martins et al.[11]

In their method V_0 is adjusted to optimize k-independence of the derived

nearest-neighbor distance. We have adapted both methods for Fourier-

analyzing the NPD, $\chi(k)$ curves, with similar results. The backscattering

phase shift $\phi_b(k)$ and amplitude $A_b(k)$ dependence were eliminated before

the transform; i.e.,

$$F(r) = \frac{1}{2\pi} \int \left[\frac{\chi(k)e^{-i\phi_b(k)}}{A_b(k)} \right] e^{-i2kr} g(k)dk \qquad (1)$$

The $\phi_b(k)$ and $A_b(k)$ values calculated by Teo and Lee[12] for Ni were used.

The square window function $g(k)$ was chosen to select a data range whose

cutoff points fell at nodes in $\chi(k)$, and the lower limit was generally

chosen to be above 100 eV kinetic energy, where the theory used to

calculate the I/E curve is on firm ground.

Fig. 1(b) shows $F(r)$ according to Eq. 1 of the $\chi(k)$ shown in Fig. 1(a). The value of V_o was set at 0 eV, which optimized the match of $F(r)$ with $\mathrm{Im}F(r)$, as discussed above. Four prominent peaks occur in $F(r)$, at 2.83Å, 4.49Å, 6.66Å and 8.66Å. The last three peaks fall within .08Å, of distances corresponding to $d_\perp + b$, $d_\perp + 2b$ and $d_\perp + 3b$, where $d_\perp$ (=2.51Å) is the perpendicular distance from Se to the first Ni(111) surface layer, used for calculating $\chi(k)$ in Fig. 1(a) and b (=2.033Å) is the interlayer spacing in Ni(111). The first peak falls at a distance which is larger by 0.32Å than the structural value of $d_\perp$ = 2.51Å used in calculating $\chi(k)$ in Fig. 1(a). A similar discrepancy in the position of the first peak only occurs in $F(r)$ derived via Eq. (1) from $\chi(k)$ curves calculated using $d_\perp$ = 2.22Å and 1.93Å for the same $\sqrt{3} \times \sqrt{3}$ R30° Se(3d) - Ni(111) system. Figure 3 shows the distances Z_F, derived from $F(r)$, plotted against the input "structural" distances Z_S for all three $d_\perp$ values. We conclude from this plot that:

1. The agreement between Z_F and Z_S is excellent for the 2nd, 3rd, and 4th interplanar distances; i.e., $d_\perp + nb$, with n = 1,2,3. A least-squares fit through these nine points gives a slope of 1.010 and an intercept of 0.012Å.

2. The first interplanar distance, $d_\perp$, is high by about 0.3Å in all three cases. Among the possible reasons for this discrepancy are effects of multiple scattering, and the choice of $g(k)$.

3. Of most importance, the derivatives of Z_F with respect to Z_S are near unity, and the dominant peaks in Z_F arise only from normal inter-planar distances. Thus Z_F faithfully yields these distances and no others.

A parallel analysis for the p(2x2) Se/Ni(001) system is illustrated in Fig. 2, and Fig. 4 shows Z_F plotted against Z_S. In this case V_0 was optimized at 5 eV. Fig. 2b shows F(r), for which the second peak (at 3.65Å) and the third peak (at 5.56Å) agree within 0.1Å with the Z_S values for $d_\perp$+b and $d_\perp$+2b, with $d_\perp$ = 1.94Å and b = 1.76Å for Ni(001). The first peak lies at 2.10Å, or 0.16Å above $d_\perp$. The broad peak at ∿7Å does not correspond well to $d_\perp$+3b, and corresponding peaks for other $d_\perp$ values are also misshapen. They were omitted from Fig. 4. With these qualifications the p(2x2) Se/Ni(001) results were similar to those for the Ni(111) face. The remarkably close agreement between Z_F and Z_S for the two structures (six cases, or 21 points in all) needs no further comment. These results suggest that it is probably possible--given good data and careful analysis--to derive $d_\perp$ values (probably from the 2nd and 3rd peaks) accurate to ∿2% by Fourier transformation of NPD data. In fact a Fourier transform analysis of NPD data from oxygen and sulfur overlayers on Ni(001) support this conclusion.[9]

In comparing Fourier-transform NPD with surface EXAFS, a complementarity is obvious: the determination of both $d_\perp$ from NPD and the nearest-neighbor distance from surface EXAFS would be especially desirable. NPD has the advantages over surface EXAFS that $\chi(k)$ is about an order of magnitude larger and that there is no contribution to the interference term from the source atom phase shift, which cancels in the direct and scattered waves.[13]

It seems clear that Fourier transformation of NPD I/E curves will yield normal interplanar spacings. In seeking a qualitative explanation, we note that lattice symmetry implies a necessary energy degeneracy between

(for example) electronic states propagating in the (100) and the ($\bar{1}$00) directions. Elastic scattering from one to the other is allowed. In contrast the needed degeneracy would in general be absent for oblique elastic scattering. Thus scattering of photoelectrons from a state propagating normally into the substrate into one propagating normally outward is favored. Therefore, the magnitude of photoelectron diffraction modulations is greater by a factor of 3-5 for normal emission as compared to non-normal emission.[14] Further tests are needed, including experimental data sets extending to high kinetic energies.

Acknowledgements

References

1. A. Liebsch, Phys. Rev. Lett. 32, 1203 (1974); Phys. Rev. B 13, 544 (1976).

2. S. Kono, C.S. Fadley, N.F.T. Hall, and Z. Hussain, Phys. Rev. Lett. 41, 117 (1978).

3. D.P. Woodruff, D. Norman, B.W. Holland, N.V. Smith, H.H. Farrel, and N.M. Traum, Phys. Rev. Lett. 41, 1130 (1978).

4. S.D. Kevan, D.H. Rosenblatt, D. Denley, B.-C. Lu, and D.A. Shirley, Phys. Rev. Lett. 41, 1565 (1978).

5. C. H. Li and S. Y. Tong, Phys. Rev. Lett. 42, 901 (1979).

6. E.A. Stern, Phys. Rev. B 10, 3027 (1974).

7. C.H. Li and S.Y. Tong, Phys. Rev. Lett. 43, 526 (1979).

8. S.D. Kevan, Ph.D. thesis, Lawrence Berkeley Laboratory Report LBL-11017, May 1980 (unpublished).

9. D.H. Rosenblatt, J.G. Tobin, M.G. Mason, R.F. Davis, and D.A. Shirley, Lawrence Berkeley Laboratory Report LBL-11447, September 1980, submitted to Physical Review B.

10. P.A. Lee and G. Beni, Phys. Rev. B 15, 2862 (1977).

11. G. Martins, P. Rabe, N. Chwentner, and A. Werner, Phys. Rev. B 17, 1418 (1978).

12. B.K. Teo and P.A. Lee, J. Amer. Chem. Soc. 101, 2815 (1979).

13. P.A. Lee, Phys. Rev. B 13, 5261 (1976).

14. S.D. Kevan, D.H. Rosenblatt, D.R. Denley, B.-C. Lu, and D.A. Shirley, Phys. Rev. B 20, 4133 (1979).

Figure Captions

Figure 1. (a) Theoretically calculated normalized NPD intensity versus k
for $(\sqrt{3} \times \sqrt{3})$ R30° Se(3d) - Ni(111) with $d_\perp$ = 2.51Å and inner
potential V_0 = 0 eV. (b) Magnitude of the Fourier transform
$|F(r)|$ according to Eq. (1) of the data in (a). Schematic
representation of the adsorption geometry is shown in the inset.

Figure 2. Same as Fig. 1, except showing p(2x2) Se(3d) - Ni(001) system
with $d_\perp$ = 1.94Å and V_0 = 5 eV.

Figure 3. Fourier-transform derived distances Z_F plotted against input
structural distances Z_S for three $d_\perp$ values of 1.93Å (circles),
2.22Å (triangles), and 2.51Å (squares) (see inset in Fig. 1 (b)).
A linear curve with slope = 1.0 is drawn to facilitate comparison
between Z_F and Z_S.

Figure 4. Same as Fig. 3, except for three $d_\perp$ values of 1.55Å (circles),
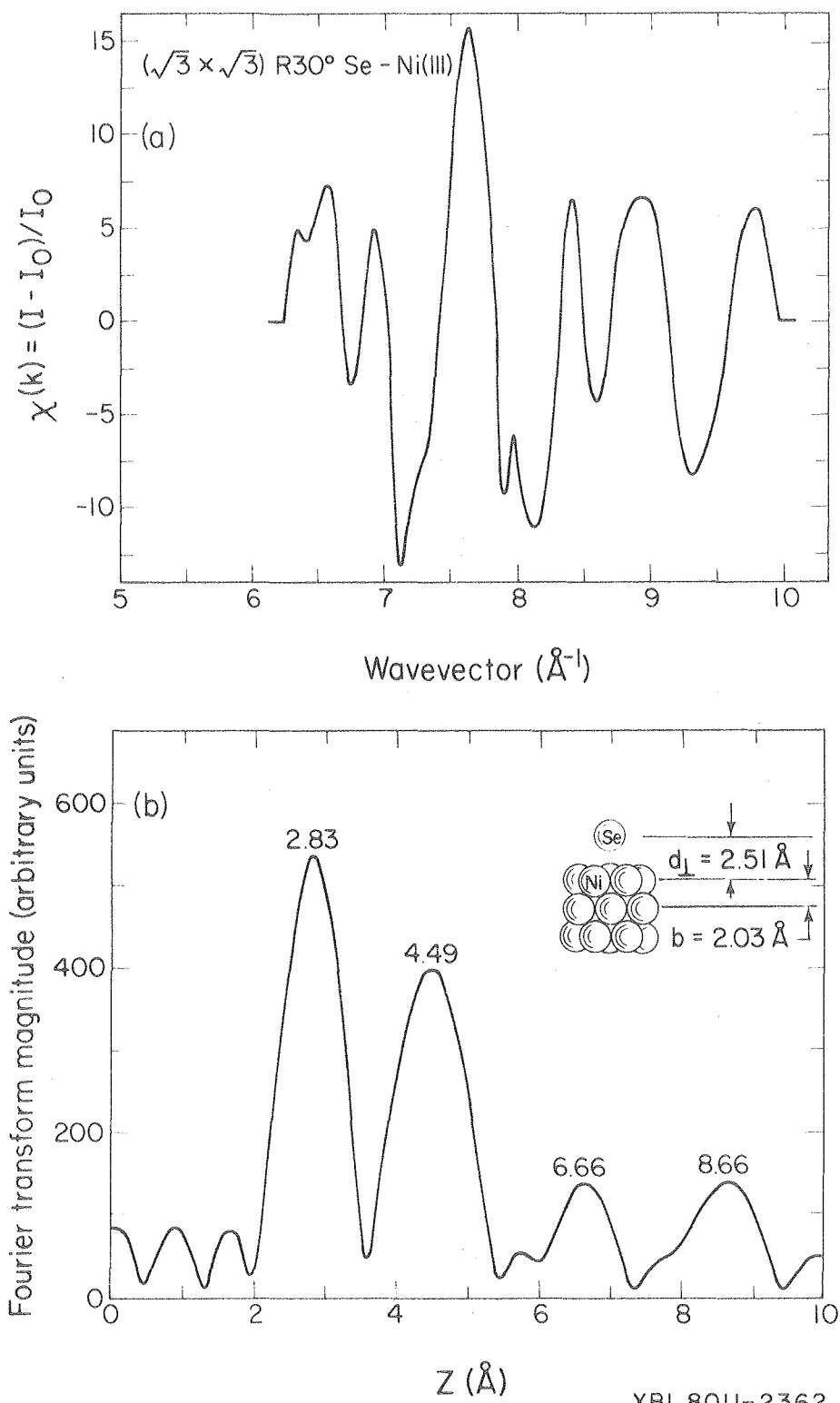1.94Å (triangles) and 2.34Å (squares) (see inset in Fig. 2 (b)).

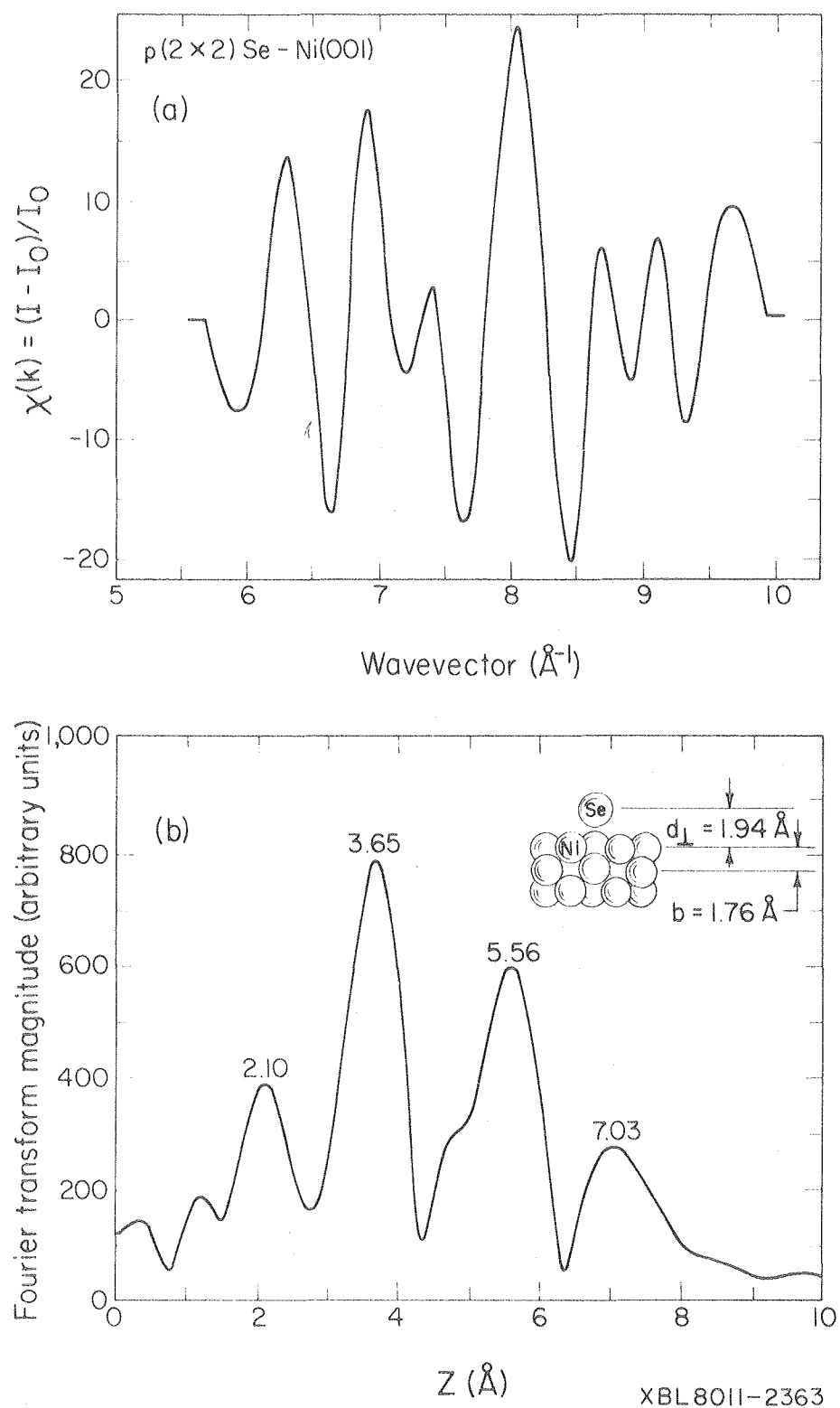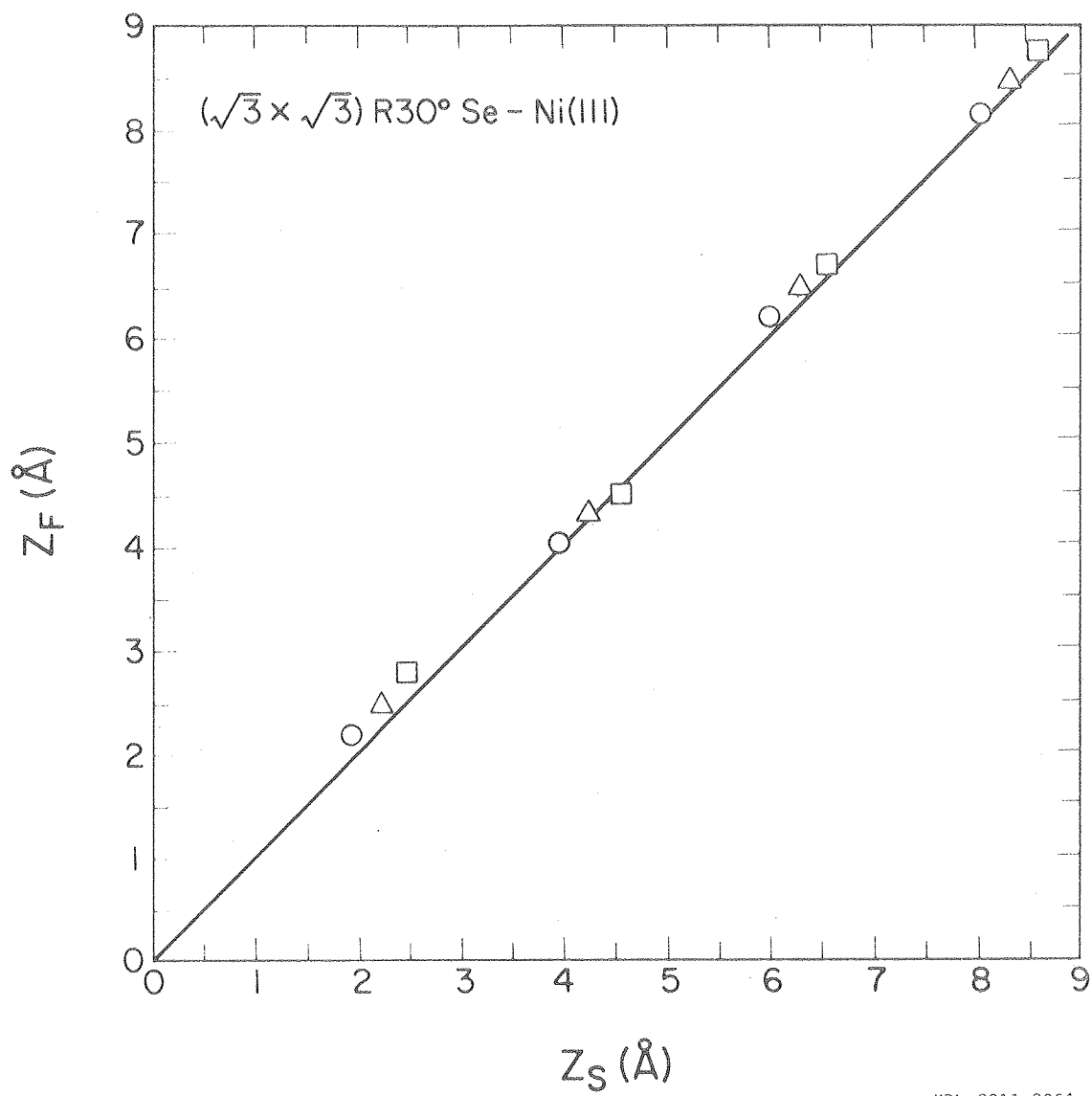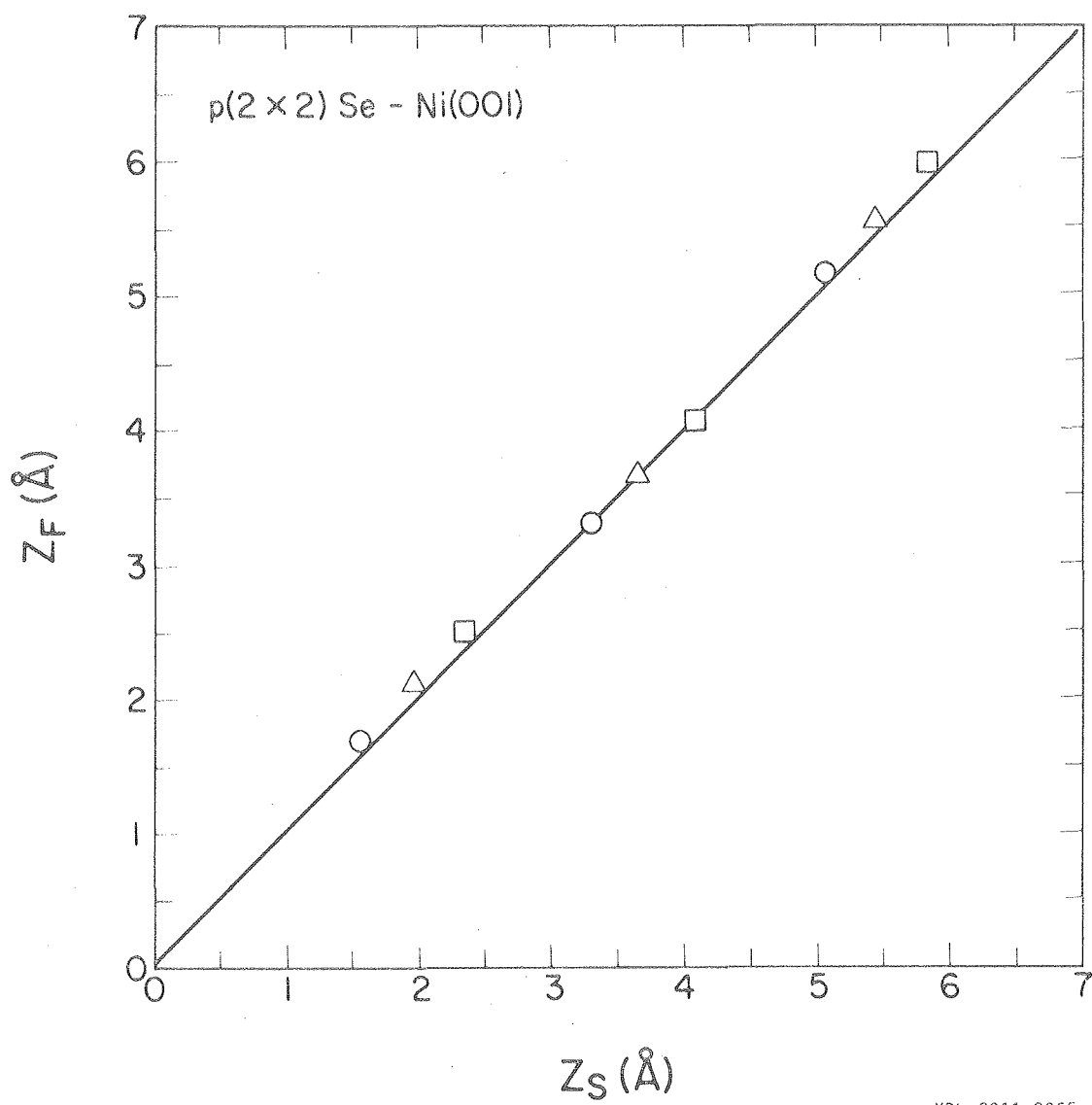$(\sqrt{3} \times \sqrt{3})$ R30° Se – Ni(III)

(a)

$\chi(k) = (I - I_0)/I_0$

Wavevector (Å^{-1})

(b)

2.83

4.49

6.66

8.66

Fourier transform magnitude (arbitrary units)

(Se)

$d_\perp = 2.51$ Å

Ni

$b = 2.03$ Å

Z (Å)

XBL 8011–2362

Figure 1

Figure 2

XBL8011-2363

$(\sqrt{3} \times \sqrt{3})\,R30°\,Se - Ni(III)$

Figure 3

XBL 8011-2364

Figure 4

XBL 8011-2365